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Some Properties of Pyrophyllite as a Pressure Medium

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Characteristics of pyrophyllite used as a pressure medium have been investigated in a pressure range of 0-100 kbar by applying a multianvil high-pressure device. The refractive index of pyrophyllite decreases when the applied pressure increases. This result corresponds to the report by Lees who found the decreased density of pyrophyllite under compression. To understand this superficially unreasonable phenomenon, deformations of the structure were studied by means of electron microscopy. At a pressure of 100 kbar, some of the layered structure of pyrophyllite appear in a massive form which may result in loss of zeolitic water molecules, but no constitutional variation in the layer was found at this pressure.

INTRODUCTION

Many differences in the construction of high-pressure apparatus are the proof of attempts to overcome the difficulty imposed by the properties of materials on compression. Especially the limitations imposed by the properties of a pressure medium used at the innermost section of the massive support in a high-pressure apparatus are so often decisive that investigations of the properties of the medium are important.

Pyrophyllite, $Al_4(Si_8O_{20})(OH)_4$, is widely used as a pressure medium due to the following properties; (a) soft mineral which is easy to process, (b) the coefficient of friction is proper to form a gasket under a high pressure and to prevent outflow of the inside material, and (c) it has good thermal and electrical insulating properties.

As one of the fundamental properties of pyrophyllite, changes in the density under a high pressure have been studied by Carte[1] and Lees.[2] According to Carte, the density of bulk pyrophyllite changes from 2.74 g/cm^3 to 2.65 g/cm^3 on compression. Lees also showed that the density of pyrophyllite compressed at 140 tons in a tetrahedral high-pressure device decreases from 2.70 ± 0.01 g/cm^3 to 2.68 ± 0.02 g/cm^3. These results appear superficially unreasonable, because they indicate that the average density of pyrophyllite decreases on compression. Lees explained the decrease by the following reasons; (a) there is a permanent density increase in the central region of the pressure medium, and (b) by much deformation of pyrophyllite near the edges, the density decreases and may over-compensate for the density increase in the central region.

By the use of an eight-anvil high-pressure apparatus developed by Kawai[3] and modified in some details, we studied changes in the refractive index, instead of the density, of the compressed pyrophyllite by the immersion method. In order to

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check the explanation proposed by Lees, observations of the structure by means of electron microscopy were also performed.

SAMPLE PREPARATION

The high-pressure device used to prepare the compressed pyrophyllite consists of eight anvils, three cylinders, and an iron frame housing the cylinders. The details of the construction are previously reported.[4,5] Since the top of the tungsten carbide section of each anvil is truncated so as to have a front face of an equilateral triangles having sides of 1.8 mm, an octahedral hollow space is formed at the center when all anvils are assembled. In the hollow space is inserted the octahedron of pyrophyllite with edges of 4.0 mm. When the oil pressure in the cylinders is elevated, the cones, which consist of eight anvils with small spacers between them, are squeezed. The octahedral pyrophyllite is then compressed and part of it becomes a gasket between the neighboring anvils thereby preventing outflow of the inside material. Several kinds of samples are prepared, where the pressure assigned on the samples is 20, 40, 60, 80, and 100 kbar, respectively. The compressed pyrophyllite is carefully taken out from the apparatus and the gasket is removed from the medium. Thus, we can get the octahedral samples with edges of about 2 mm.

The samples prepared by the procedure described above are then used to measure the refractive index and to observe the structure by electron microscopy.

MEASUREMENT OF REFRACTIVE INDEX

Carte[1] and Lees[2] reported independently that the density of pyrophyllite decreases on compression. These results seem to be unreasonable, because any material decreases, more or less, its volume on compression, which results in the increased density. Since measurements of the refractive index is expected to be more sensitive than measurements of the density variation for pyrophyllite with the main constituent

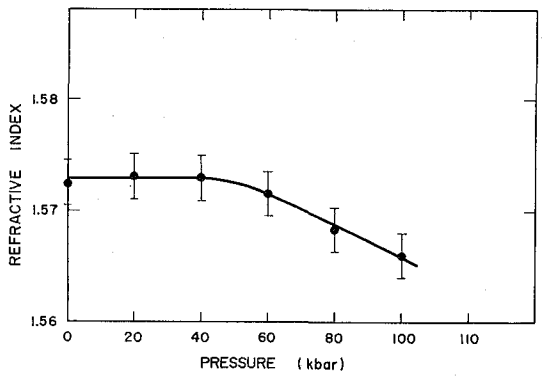


Fig. 1. Changes in the refractive index of the octahedral pyrophyllite on compression. Each sample is powdered and the index is measured by the immersion method.

of some schistose rocks, the octahedral pyrophyllite compressed was powdered to a diameter of about 50 μ and the refractive index was determined by the immersion method.

The liquid employed in the measurement is a homogeneous mixture of alpha–Bromonaphtalene and Bromobenzene, of which ratio is changed to get the mixture with different refractive indexes. The powdered sample was immersed in the liquid with various known refractive indexes and the Becke line appeared around the sample with the D line of Na (589 mμ) was observed. When the Becke line disappeared, the refractive index of the liquid in question was measured and the value of the index was assigned as that of the sample. To secure the results, the measurement of the index was repeated. The average value of the indexes is shown in Fig. 1 as a function of loaded pressures. The figure reveals that the refractive index of pyrophyllite decreases as the pressure increases. The present result can be said to correspond to the previous reports for the density change by Carte[1] and Lees.[2]

For better understanding of this phenomenon, observations of the structure of pyrophyllite by means of electron microscopy was performed.

DEFORMATION OF THE STRUCTURE

Pyrophyllite is a soft mineral (schistose rock) which often appears in hydrothermal vein. The structure of pyrophyllite has been investigated by Pauling,[6] Gruner,[7] and Hendricks.[8] More recently, study on the structure by electron diffraction was performed by Zvyagin and Pinsker.[9] By these works, it has been revealed that pyrophyllite has a layered structure in which octahedrally coordinated Al ions are sandwiched between SiO_4 tetrahedra.

It is certain that zeolitic water molecules contained in pyrophyllite can be removed below 600°C. By heating at higher temperatures, the constitutional water of pyrophyllite can be removed. According to Kiefer,[10] the dehydration begins at 640°C and rapid dehydration occurs in the temperature range of 690–780°C. At 850°C, the dehydration ends.

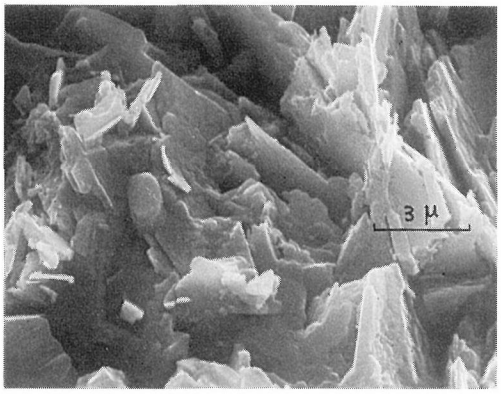
Carte[1] measured variations in density of pyrophyllite after heating to various temperatures and found that the density decreases almost linearly from 2.66 to 2.38 in the temperature range of 400–900°C. This result seems to correspond to the above mentioned results on loss of zeolitic and constitutional water.

In order to understand the decreased refractive index of pyrophyllite on compression described in the previous section, we studied the structure by means of electron microscopy. The observations were performed in two ways.

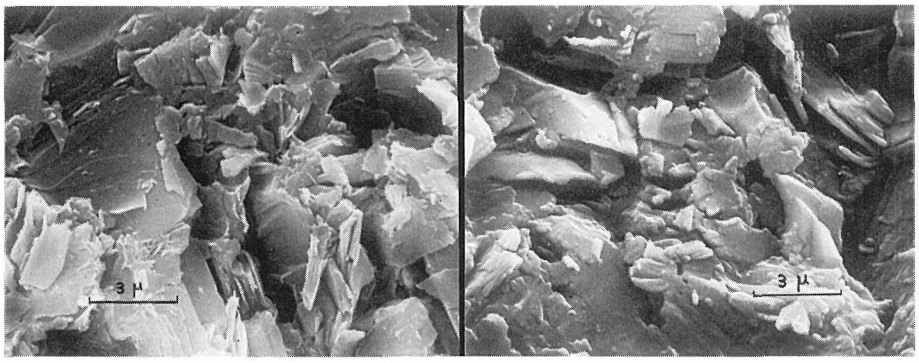
Firstly, the octahedral samples prepared were devided into two pieces and the larger surfaces were covered by vacuum evapolated gold films. By the use of a scanning electron microscope, the surface of the samples were observed.

In Figs. 2 a-e, are shown some of the observed pictures which include those of the uncompressed natural pyrophyllite (Fig. 2 a), of the compressed at 20 kbar (Figs. 2 b and c), and of the compressed at 100 kbar (Figs. 2 d and e). From the observations we get the following conclusions; (a) uncompressed natural pyrophyllite has a layered structure and has a high degree of disorder in the crystal structure indicating

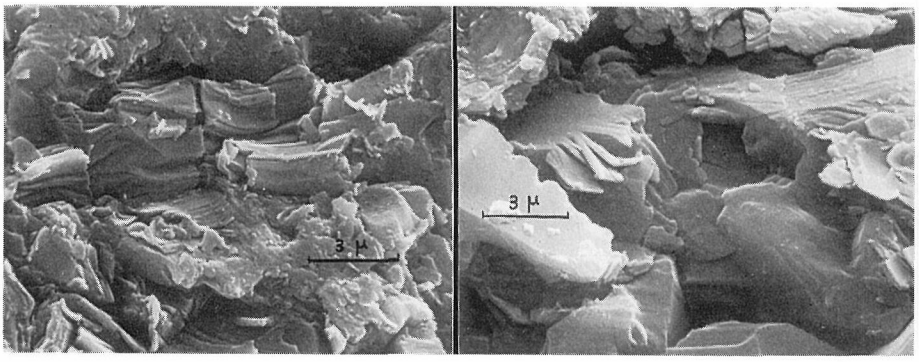
a weak bonding between neighboring layers, (b) at a pressure of 20 kbar, some of the layers are spalled, but the pressure medium still holds the layered structure, and (c) at a pressure of 100 kbar, deformation of the layered structure is appreciable in both parts, center and edge, of the octahedron and some of the layers appear in a massive form.



(a)

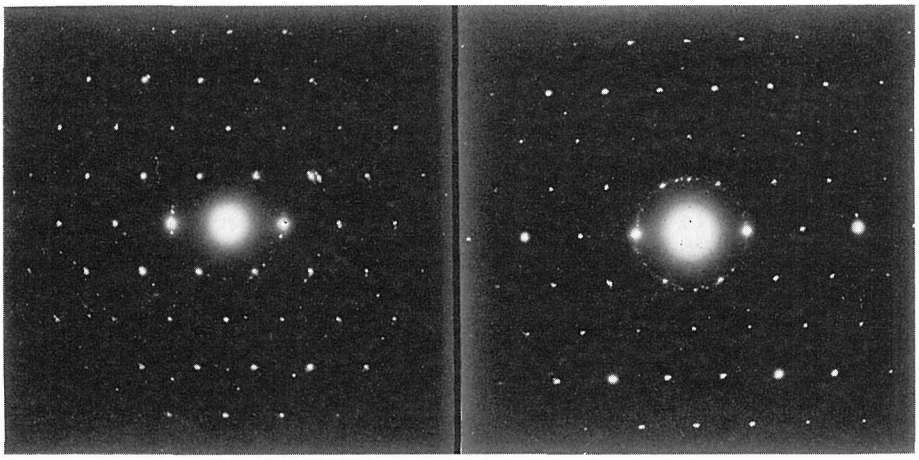


(b) (c)



(d) (e)

Fig. 2. Structure of pyrophyllite observed by a scanning electron microscope; a) the uncompressed natural pyrophyllite, b) the compressed at 20 kbar (central part of the octahedron), c) the compressed at 20 kbar (edge of the octahedron), d) the compressed at 100 kbar (central), e) the compressed at 100 kbar (edge).



(a) (b)

Fig. 3. Structure of pyrophyllite observed by means of electron diffraction; a) the uncompressed natural pyrophyllite, b) the compressed at 100 kbar.

In addition to observations of the structure by a scanning electron microscope, the electron diffraction pattern of the samples was observed to see the inner structure of the layer. Two kinds of samples, uncompressed and compressed at 100 kbar, were powdered and then soaked in distilled water. After five hours, the supernatant sample was taken on a mesh to use in an electron microscope, in which the electron beam was irradiated perpendicularly to the (001) plane. If there is any appreciable deformations in the constituent of the crystal, the electron diffraction should appear in different patterns. However, as indicated in Figs. 3 a and b, comparisons of both patterns corresponding to the uncompressed and the compressed, no distinguishable variation was found.

From the results, one can conclude that at a pressure of 100 kbar, some of the layered structure become bulky, but no observable deformation takes place in the constituent of the crystal.

DISCUSSION

In the present work it became evident that the characteristics of pyrophyllite as a pressure medium do not change essentially below 100 kbar, although some of the disordered layers become massive. However, from the investigation with the compressed pyrophyllite by using an electron microscope, it was revealed that explanations proposed by Lees[2] on the decreased density of pyrophyllite under a high pressure is not appropriate, because no constitutional variation takes place even at 100 kbar.

One possibility left to understand the decreased density on compression is that the decrease is attributed to loss of zeolitic water molecules contained in pyrophyllite, *i.e.*, loading a pressure on the crystal may cause the same effect as heating in view of density. But taking into consideration the present result on the refractive index, there still be some doubt for this explanation.

In order to settle this subject, more refined study of the structure by X-ray diffraction is hoped.

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